



# Hydrothermal carbonization and torrefaction of grape pomace: A comparative evaluation



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## HIGHLIGHTS

- Chars were produced from grape pomace by hydrocarbonization and torrefaction.
- Fuel qualities of hydrochars were compared to pyrochars.
- Hydrochars have higher combustion reactivity than pyrochars.
- Waste solution from hydrocarbonization shows antioxidant activity.

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## ABSTRACT

Grape pomace was treated by hydrothermal carbonization (sub-critical water, 175–275 °C) and torrefaction (nitrogen atmosphere, 250 and 300 °C), with mass yield of solid product (char) ranging between 47% and 78%, and energy densification ratio to 1.42–1.15 of the original feedstock. The chars were characterised with respect to their fuel properties, morphological and structural properties and combustion characteristics. The hydrothermal carbonization produced the char with greater energy density than torrefaction. The chars from torrefaction were found to be more aromatic in nature than that from hydrothermal carbonization. Hydrothermal carbonization process produced the char having high combustion reactivity. Most interesting was the finding that aqueous phase from hydrothermal carbonization had antioxidant activity. The results obtained in this study showed that HTC appears to be promising process for a winery waste having high moisture content.

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## 1. Introduction

The biomass is abundant in nature and is a clean and renewable energy source. Biomass is transferred to different forms of energy by the thermochemical and biochemical processes. Biomass energy is a growing source of energy around the world. It can be produced from many types of organic matter and reduces the dependence on foreign oil, improve air quality, and support rural economies. But some specific properties of biomass, such as high volatile content, high oxygen content, existing in many diverse forms, low density and high water content are the major drawbacks to employ it as an energy feedstock. Because of this, pre-treatment technologies are needed to convert the biomass into a solid fuel, which provides a more suitable feedstock for further thermochemical conversion

processes, such as combustion/co-combustion and gasification. The carbonization of biomass at low temperatures improves not only energy content of biomass, but also its properties for easier handling, transport and storage. Additionally, carbonized biomass is easily grindable, leading to a more uniform feed for further thermochemical processing. Two different low temperature carbonization processes are used to increase the energetic use of biomass waste: hydrothermal carbonization and torrefaction.

The torrefaction is a low-temperature pyrolysis, in which the biomass is heated in an inert gas environment at temperatures ranging from 200 to 350 °C. Numerous works has been done on analysis of the products of torrefaction for different feedstocks and process conditions (Almeida et al., 2010; Arias et al., 2008; Bridgeman et al., 2008; Medic et al., 2012; Lee et al., 2012; Medic et al., 2012). Generally, 80–95% of the energy and 70–90% of the mass of the biomass is retained in the torrefied product (char) (Bates and Ghoniem, 2012). However, conversion of biomass to char via torrefaction is been restricted to biomass with low water

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content, such as wood and crop residues, because of the high energy requirements due to the necessity of pre-drying process.

On the other hand, hydrothermal carbonization is a promising technology for biomass having high water content (up to 80%). The term 'hydrothermal carbonization' refers to the formation of a solid residue by applying temperatures of 180–250 °C in a suspension of biomass and water at saturated pressure. A number of studies have been performed on hydrothermal carbonization covering a wide range of biomass feedstock, such as loblolly pine (Yan et al., 2009), wood meal (Kang et al., 2012), palm empty fruit bunches (Parshetti et al., 2013), sewage sludge (He et al., 2013), Coconut fiber and dead eucalyptus leaves (Liu et al., 2012), eucalyptus sawdust and barley straw (Sevilla et al., 2011), swine-manure (Cao et al., 2011), digested maize silage (Mumme et al., 2011), a mix of Jeffrey Pine and White Fir (Hoekman et al., 2011) walnut shell and sunflower stem (Román et al., 2012). Hydrothermal carbonization is an exothermic process and results in three products; gases, aqueous chemicals, and a solid fuel (hydrochar) (Yan et al., 2009). The mechanisms of hydrothermal carbonization are associated with a series of hydrolysis, condensation, decarboxylation, and dehydration reactions (Lu et al., 2012). In comparison to torrefaction, hydrothermal carbonization offers the advantage of converting wet biomass into carbonaceous solids at relatively high yield, without a energy intensive drying process. In addition, a considerable amount of inorganics in biomass is dissolved in hot compressed water, leading to production of hydrochar with low ash content. However, most of inorganics retain in the resultant pyrochar in torrefaction.

Wine is a popular and important beverage with 252 million hectolitres produced in 2012 (<http://www.oiv.int>). The wine industry generates huge amounts of grape pomace as an industrial waste, accounting for 20–25% of the grape used in wine production (Yu and Ahmedna, 2013), with disposal an important environmental consideration. On the other hand, grape pomace consists of seeds, skins and stems, and it is a rich source of phenolic compounds, both flavonoids and non-flavonoids. It can be used as animal feed, fertilizer or feedstock for antioxidants. But, it has high moisture content (>60%) and a significant amount of energy is needed for drying before use. These characteristics make it an interesting feedstock for hydrothermal carbonization. In the present study, the hydrothermal carbonization of grape pomace is investigated for the first time. The influence of temperature and time on yield and properties of char was tested. For comparison purpose, dry torrefaction of grape pomace was also carried out. Characterization of chars which includes fuel properties,

morphological and structural properties and combustion characteristics was performed.

## 2. Methods

### 2.1. Material

Grape pomace (GP) having 50 wt% of initial moisture was kindly provided by a local winery (Yazgan Sarapçilik., Izmir). Received GP was previously dried at room temperature (25 °C) for 72 h, then in a drying oven at 60 °C for 24 h. Dry GP samples were ground and sieved through 1.0 mm sieve in order to provide homogeneity of the biomass for the experiments, then they were stored in sealed containers until use. The results of ultimate and proximate analysis of grape pomace are shown in Table 1.

### 2.2. Experimental procedure

Hydrothermal carbonization experiments (HTC) were conducted in a 100 ml stainless steel shaking autoclave. Biomass and de-ionized water mixture (1:4 biomass/water ratio) was loaded into the reactor and then the reactor temperature was increased to desired temperature (175–275 °C) at a heating rate of 5 °C min<sup>-1</sup>. The reactor was held at final temperature for required reaction times (10, 30 and 60 min) and then cooled rapidly to room temperature. The effect of reaction time on the process was investigated at 225 °C with various reaction times (10, 30 and 60 min). Resulting hydrochars and aqueous phases were separated by filtration. Hydrochars were first washed with de-ionized water and then dried in an oven at 105 °C for 24 h, while aqueous phases were bottled and kept at 4 °C until further analysis.

For comparison, torrefaction experiments were also performed at 250 and 300 °C temperatures with a reaction time of 30 min. Torrefaction experiments were carried out in a stainless steel 1 L vertical reactor which was a fixed bed design. In a typical run, 50 g of GP was placed into the reactor and then the system was heated to the desired temperature under N<sub>2</sub> atmosphere at a heating rate of 5 °C min<sup>-1</sup>, and held at this temperature for 30 min. Resulting char products were dried in an oven at 105 °C for 24 h and then stored in sealed containers until further analysis.

Char samples were named as following the "Process–Temperature–Time" sequence (e.g. H-225-10 stands for hydrothermal carbonization conducted at 225 °C for 10 min, whereas T-250-30 stands for torrefaction conducted at 250 °C for 30 min).

**Table 1**

Proximate analysis, ultimate analysis and heating value of grape pomace and derived hydrochars/biochars.

| Sample          | Proximate analysis, % |      |      | Elemental analysis, % |      |      |                | HHV (MJ/kg) | ED   | EY (%) |
|-----------------|-----------------------|------|------|-----------------------|------|------|----------------|-------------|------|--------|
|                 | VM                    | Ash  | FC   | C                     | H    | N    | O <sup>a</sup> |             |      |        |
| GP              | 72.6                  | 5.4  | 21.9 | 49.10                 | 6.30 | 2.29 | 42.31          | 20.04       | –    | –      |
| H-175-30        | 69.3                  | 1.4  | 29.2 | 58.64                 | 6.21 | 2.19 | 32.95          | 24.32       | 1.21 | 73.89  |
| H-200-30        | 67.7                  | 1.1  | 31.3 | 60.16                 | 6.11 | 1.72 | 32.01          | 24.84       | 1.24 | 74.90  |
| H-225-10        | 67.1                  | 1.9  | 30.9 | 61.39                 | 6.40 | 1.72 | 30.49          | 25.75       | 1.29 | 77.40  |
| H-225-30        | 64.6                  | 1.7  | 33.7 | 61.87                 | 6.14 | 1.79 | 30.20          | 25.65       | 1.28 | 75.35  |
| H-225-60        | 64.6                  | 2.1  | 33.2 | 63.05                 | 6.31 | 1.87 | 28.77          | 26.40       | 1.32 | 76.43  |
| H-250-30        | 58.6                  | 3.4  | 37.9 | 65.89                 | 5.80 | 2.17 | 26.13          | 27.03       | 1.33 | 68.93  |
| H-275-30        | 54.3                  | 2.7  | 43.0 | 68.32                 | 5.92 | 2.32 | 23.45          | 28.31       | 1.42 | 66.03  |
| T-250-30        | 63.9                  | 8.2  | 27.8 | 55.92                 | 6.35 | 2.20 | 35.50          | 23.12       | 1.15 | 89.81  |
| T-300-30        | 51.2                  | 10.5 | 38.2 | 62.90                 | 5.41 | 2.65 | 29.04          | 25.29       | 1.26 | 74.11  |
| TM <sup>b</sup> | –                     | –    | –    | 70.06                 | 5.19 | 0.10 | 23.42          | 28.26       | 1.39 | 70     |
| CF <sup>c</sup> | 67.9                  | 5.0  | 27.1 | 67.10                 | 5.20 | 0.98 | 26.43          | 26.7        | 1.45 | 65.70  |
| EL <sup>c</sup> | 70.1                  | 6.9  | 23.0 | 62.30                 | 5.47 | 1.44 | 30.35          | 25.0        | 1.32 | 61.12  |

VM: volatile matter, FC: fixed carbon, ED: energy densification, EY: energy yield.

<sup>a</sup> Calculated by difference.

<sup>b</sup> Hydrochar from Tahoe mix (Jeffrey pine + White Fir) at 255 °C for 30 min (Hoekman et al., 2011).

<sup>c</sup> Hydrochar from coconut fiber (CF) and dead eucalyptus leaves (EL) at 250 °C for 30 min (Liu et al., 2013).

To avoid confusion, the term “hydrochar” is used when referring to the char produced from hydrothermal carbonization process, whereas the term “pyrochar” is used for the char produced from torrefaction process.

### 2.3. Product characterization

The elemental compositions of grape pomace and chars were determined by using an elemental analyzer (LECO CHNS 932) according to ASTM D3176-89. The higher heating values (HHV) of grape pomace and chars were calculated according to following formula (Channiwala and Parikh, 2002);  $\text{HHV} = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0221\text{A}$ .

Proximate analysis was determined according to ASTM D3174-04 for ash analysis and ASTM D3175-89 for volatile matter. The infrared spectrum was recorded with a Perkin Elmer FT-IR coupled with Attenuated total reflectance (ATR). Thermal degradation behaviour of grape pomace and chars was investigated in a thermogravimetric analyser (Perkin Elmer Diamond TG/DTA) under  $\text{N}_2$  atmosphere with a flow rate of  $200 \text{ mL min}^{-1}$  and a heating rate of  $10^\circ\text{C min}^{-1}$ . The combustion characteristics of GP and chars were determined by the same thermogravimetric analyzer under air atmosphere with a flow rate of  $100 \text{ mL min}^{-1}$  and a heating rate of  $20^\circ\text{C min}^{-1}$ . The scanning electron microscopy (SEM) analyses were performed by JSM-6060 JEOL instrument.

A commercial TOC analyser (HachLange IL550-TOC-TN) was used to determine the residual total organic carbon (TOC) content in the aqueous phase. Antioxidant activities of the aqueous phases were determined according to DPPH-radical scavenging capacity method, which was developed by Brand-Williams et al. (1995) and expressed as milligrams of gallic acid (GA) equivalents per liter aqueous solution.

## 3. Results and discussion

### 3.1. Char yields and carbon distribution

A series of HTC experiments were carried out to determine the effects of the reaction temperature and hold time on the treatment of grape pomace. In the first set of experiments, a range of reaction

temperatures was used from 175 to  $275^\circ\text{C}$  while the hold time was kept constant at 30 min. In the second set of experiments, the reaction temperature was held constant at  $225^\circ\text{C}$ , while the hold time was varied from 10 to 60 min. The variations in char yields defined as the mass ratio of dry char products to dry grape pomace are shown in Fig. 1.

Hydrochar yields followed a decreasing trend with the increasing temperature as shown in Fig. 1. Yields were in the range of 46.5–61.1 wt% which are similar to the results found in literature (Hoekman et al., 2011; Liu et al., 2012). This is consistent with the enhancement of decomposition of grape pomace and/or secondary decomposition of hydrochar which leads to gasification and liquefaction reactions at higher temperatures. Varying reaction time of the process at  $225^\circ\text{C}$  had a small effect, as the reaction time increased from 10 to 60 min hydrochar yields only decreased from 60.0 to 57.9 wt%. The tendencies found are consistent with some studies that carried out HTC with different biomass materials (Hoekman et al., 2011; Román et al., 2012). Under the operating conditions in this study, the temperature appears to have a stronger effect on HTC product distributions than the reaction time.

In the case of torrefaction, increasing the reaction temperature from  $250^\circ\text{C}$  to  $300^\circ\text{C}$  decreased the pyrochar yields from 78.1 to 58.8 wt%. This sharp decrease in pyrochar yield could be explained by the decomposition of cellulosic fraction of lignocellulosic biomass near  $300^\circ\text{C}$  (Ciolkosz and Wallace, 2011; Prins et al., 2006). The TG analysis of grape pomace supports this conclusion (Fig. 2a). As expected, char yields from torrefaction were higher than that of hydrothermal carbonization. In both processes, dehydration and decarboxylation are main degradation reactions. But, in addition to these reactions, during hydrothermal carbonization, extractables (both some of organics and inorganics) are also being eluted simultaneously; most of which exhibit very good solubility in subcritical water (Funke and Ziegler, 2010). Because of above reason hydrochar yields were lower compared to pyrochar yields.

In HTC process, carbon distribution among the solid, aqueous and gas phases was calculated according to elemental analysis of hydrochars and TOC analysis of aqueous phases. Thus carbon distribution in product,  $\text{wt}\% = (\text{carbon (wt\%) in product} / \text{carbon (wt\%) in GP}) \times 100$ . The carbon distribution in gas product was calculated from difference. As seen from Fig. 3, a big part of carbon

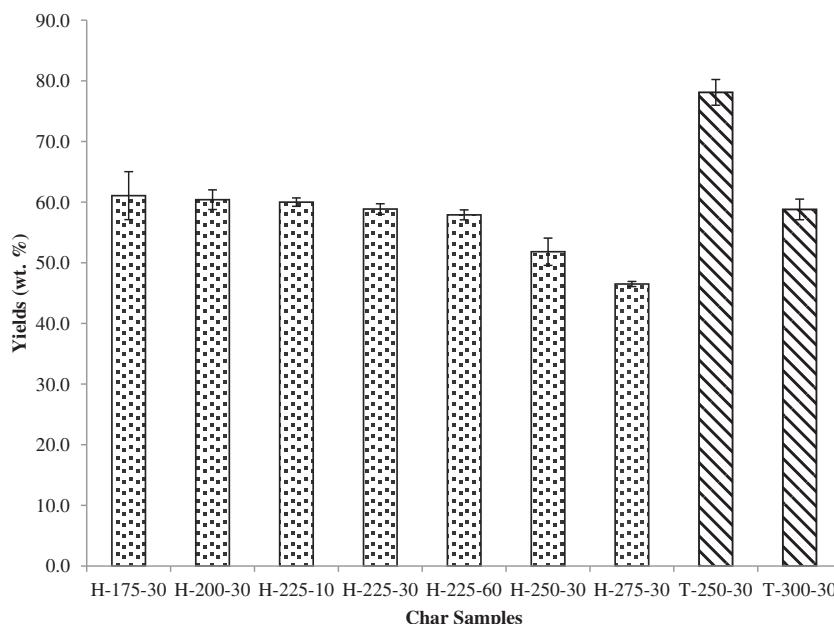


Fig. 1. Char yields for hydrothermal carbonization and torrefaction of grape pomace. Error bars represent averages  $\pm$  standard deviations.

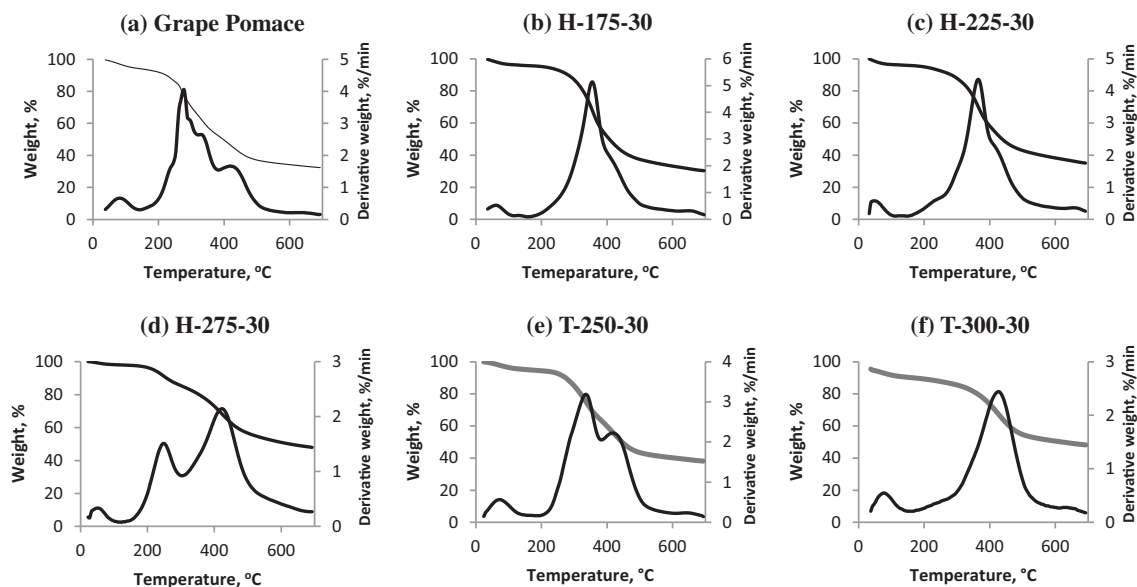


Fig. 2. TG/DTG profiles of grape pomace and derived chars under nitrogen atmosphere.

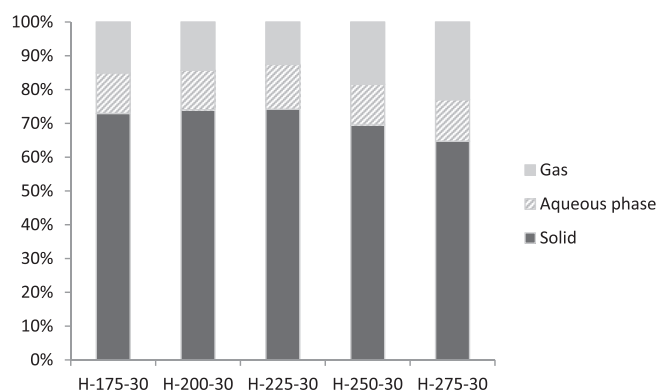


Fig. 3. Carbon distribution in hydrothermal carbonization.

in GP (65–73 wt%) was retained in hydrochar. Above 225 °C, distribution of carbon in the gas increased, indicating the increase in gas generation, mainly carbon dioxide. However, distribution of carbon in aqueous phase (around 12 wt%) did not significantly change over the temperature range of 175–275 °C.

### 3.2. Fuel characteristics of chars

Proximate analysis, elemental analysis, HHVs, energy densification ratios and energy yields of grape pomace and produced char samples are summarised in Table 1. During HTC, carbon contents of hydrochars increased substantially with the increase in temperature, oxygen contents decreased significantly and hydrogen contents changed slightly showing that carbonization took place. Torrefaction of grape pomace at 250 and 300 °C also led to an increase in carbon content. However it is less dramatic compared to HTC. The increase in carbon contents and the decrease in oxygen contents provided a char product with higher HHV which was the intended effect of both HTC and torrefaction processes to increase the energy density of the biomass. In order to investigate the differences in atomic composition of GP and derived char products, H/C and O/C atomic ratios of biomass and chars were plotted in van Krevelen Diagram (Fig. 4). As it is clearly seen HTC led to a decrease in H/C and O/C atomic ratios of chars with an increase in reaction temperature. The decrease in those ratios provides a char

product that is similar to coal. The holding time also had an effect on elemental composition, increasing the holding time provided a hydrochar with higher carbon content. The evolution of the H/C–O/C atomic ratios from the raw material to the hydrochar basically follows the trend corresponding to a dehydration process and, decarboxylation also took place at high temperature. Similar results had been observed in the hydrothermal carbonization of eucalyptus sawdust and barley straw (Sevilla et al., 2011). The hydrochars produced between 175 and 275 °C exhibited H/C ratios of 1.26–1.03 and O/C ratios of 0.42–0.26. These ratios are also different from those obtained with swine manure (H/C = 1.50, O/C = 0.57) (Cao et al., 2011), digested maize silage (H/C = 1.26, O/C = 0.24) and cellulose (H/C = 1.17 and O/C = 0.35) (Mumme et al., 2011) despite the fact that the reaction temperatures were similar. The differences may be due to the differences in raw material composition and hydrothermal process conditions (except reaction temperature). Torrefaction conducted at 250 °C produced a char product that resembles biomass since it has substantially higher H/C and O/C ratios compared to hydrochars. By considering the H/C and O/C atomic ratios of lignite which are in the range of 0.8–1.3 and 0.2–0.38, respectively (He et al., 2013). It can be suggested that chars produced was comparable to lignite.

Proximate analysis is commonly used to establish coals and other solid fuels' suitability for combustion, pyrolysis, and gasification. It can be easily concluded that both HTC and torrefaction processes decreased volatile matter content and increased fixed carbon content of grape pomace (Table 1). These processes also proved to be efficient in order to reduce the volatile matter fraction (volatile matter/volatile matter + fixed carbon) of combustible carbon inside the biomass. Volatile matter fractions of 0.55 (H-275-30) and 0.57 (T-300-30) which are close to that of coal were achieved for HTC and torrefaction processes, respectively. As known, high volatile matter content of biomass influences its direct combustion and co-combustion with coal resulting in reduced combustion performance and increased pollutant emissions (Dai et al., 2008). A large difference in the volatiles ratio between biomass and the coal leads to separated combustion region with biomass during co-combustion of biomass with coal (Liu et al., 2012).

Solubility of inorganics at subcritical water conditions led to lower ash contents in hydrochars compared to pyrochars. Similarly, Liu et al. (2012) observed a significant decrease in ash

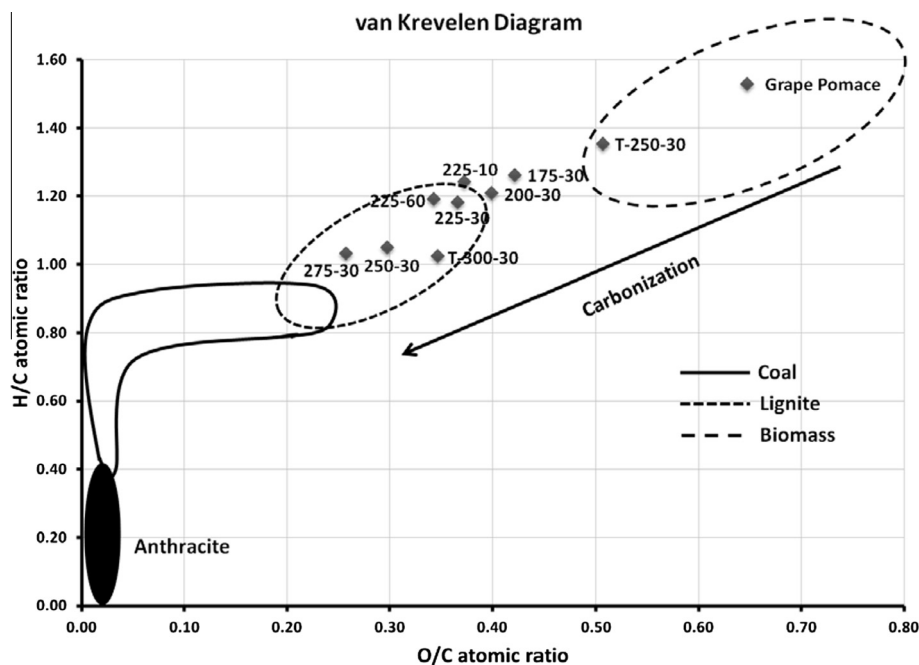


Fig. 4. Atomic H/C and O/C ratios of grape pomace and its derived-chars (coal for comparison).

content due to the dissolution of inorganics during the hydrothermal carbonization of coconut fiber and eucalyptus leaves in the temperature range of 200–300 °C (Liu et al., 2012). But they also observed an increase in ash content after 300 °C due to the decreased solubility of inorganics and subsequent precipitation.

On the contrary, torrefaction process produced a char product with higher ash content compared to grape pomace as a result of increasing fraction of inorganics in the product. These results suggest that char products produced through HTC process are more desirable than their counterparts produced through torrefaction process in terms of ash content, regarding further thermochemical conversion (combustion, gasification, pyrolysis) of the chars require low inorganics content to prevent fouling, slagging in these processes. One of the major barriers to widespread use of biomass is that biomass has a lower energy content than traditional fossil fuels, which means that more fuel is required to get the same amount of energy. Energy density is a term used to describe the amount of energy stored per unit volume. Energy densification ratio is a measure which indicates the ratio of HHV of product to HHV of raw biomass. On the other hand, energy yield is defined as fuel value of solid product (char) as a fraction of fuel value of raw biomass. Energy densification ratios and energy yields are good measures to determine the effectiveness of the carbonization process. As it is seen on Table 1, during HTC, energy densification ratios increased from 1.21 to 1.42 by increasing temperature in the temperature range of 175–275 °C, while energy yields increased slightly up to 225 °C process temperature and then decreased. It could be said that during HTC energy yields did not change significantly over the temperature range studied. The slight decrease in energy yields above 225 °C could be attributed to the decrease in mass yields of the respective hydrochars. In literature, it was reported that the energy yield of hydrothermal char from a mix of Jeffrey and White Fir varied from 70% to 77% over the temperature range of 215–295 °C (Hoekman et al., 2011). However, the energy yield from coconut fiber and eucalyptus leaves varied from 76.67% to 65.00% and 87.34% to 61.32% within the temperature range of 200–300 °C, respectively (Liu et al., 2013). The differences in biomass feedstocks could explain these

observations. Although torrefaction of GP at 250 °C yielded a pyrochar with a relatively high energy yield of 89.8%, its HHV is even smaller than the HTC char obtained at the lowest temperature studied (H-175-30 having a HHV of 24.32 MJ/kg). High energy yield should be the result of highest mass yield obtained in these processes. Obviously, HTC is more successful at energy densification. The energy content per weight of the hydrochars was ranging from 24.32 to 28.31 MJ/kg which are more than that of lignite and close to that of typical bituminous coals.

Since researches on the hydrocarbonization process systems are still in an embryo stage, a detailed economic analysis for hydrochar production from grape pomace cannot be given in this study. For meaningful process comparisons, cost of pre- and post-processing and heat recovery and auxiliary processes for by-product treatment should be considered besides the energetic nature of carbonization process. As known from literature (Libra et al., 2011; Titirici et al., 2007; Funke and Ziegler, 2010), hydrothermal processes has energetic advantage related to drying of feedstock and external heat of process. It was stated that external heat necessary for HTC is substantially lower than for the dry pyrolysis and HTC is more economical for the feedstock with a water content of more than 50% (Libra et al., 2011).

### 3.3. Morphological and structural characterization of chars

The changes in the chemical structure of the chars depending on the temperature were investigated by using Fourier transform infrared spectroscopy. The bands and the peaks in the spectrums were assigned as follows; (I) double peaks at 2920 and 2850  $\text{cm}^{-1}$ , C–H stretching vibration and deforming vibration, respectively, (II) the peak at 1743  $\text{cm}^{-1}$ , C=O stretching vibration, carbonyl and ester groups which is a characteristic peak for Xylans of hemicelluloses, (III) the peaks around 1612–1450  $\text{cm}^{-1}$ , C=C stretching of aromatic groups, (IV) the peak at 1157  $\text{cm}^{-1}$ , C–O–C vibrations in the cellulose and hemicellulose (Sevilla et al., 2011).

According to suggested assignments, (I) double peaks at 2920 and 2850  $\text{cm}^{-1}$  were present in hydrochars and grape pomace suggesting the presence of aliphatic and hydroaromatic structures, (II)

the intensity of the peak at  $1743\text{ cm}^{-1}$  decreased by increasing temperature and completely disappeared at higher temperatures (250 and  $275\text{ }^{\circ}\text{C}$ ) indicating that decomposition of hemicelluloses occurred at lower temperatures compared to that of lignin and cellulose, (III) the peaks around  $1612\text{--}1450\text{ cm}^{-1}$ , which corresponds to  $\text{C}=\text{C}$  stretching of aromatic groups of lignin, were present in all hydrochars implying that some lignin fragments and intermediate structures remained in the resulting hydrochars, e.g., lignin did not decompose completely under the hydrothermal conditions that were investigated. The intensity of (IV) the peak at  $1157\text{ cm}^{-1}$  which shows characteristics  $\text{C}-\text{O}-\text{C}$  vibrations in the cellulose and hemicellulose decreased with increasing temperature proving that cellulose also started to decompose at temperatures higher than  $250\text{ }^{\circ}\text{C}$ .

On the other hand, for pyrochars, there is a strong band at  $1463\text{ cm}^{-1}$  which is attributed to  $\text{C}_6$  ring modes (Ghani et al., 2013), shows the presence of aromatic structures. There is a newly added peak around  $1700\text{ cm}^{-1}$ , indicating that a  $\text{C}=\text{O}$  bond was formed during torrefaction process. The  $\text{C}=\text{O}$  might be a carboxyl group and/or a carbonyl group formed by dehydration of a hydroxyl group (Kang et al., 2012). The increase in intensity of the band at  $719\text{ cm}^{-1}$  which are assigned to aromatic  $\text{C}-\text{H}$  bending vibrations suggest that aromatic rings formed and/or recombined. IR spectra demonstrated that pyrochars were more aromatic in nature than hydrochars.

On the other hand, the observations from the SEM Images of GP, hydrochars and pyrochars could be summarised as follows; while raw GP showed a smooth surface due to the lignocellulosic fiber structure of the feedstock, images of hydrochars showed less smoother, uneven, heterogeneous structures due to the degradation and decomposition of cell walls in GP. Moreover, hydrothermal carbonization led to the formation of numerous carbon microspheres resulting from the recombination of degradation products during HTC (Sevilla et al., 2011). On the other hand pyrochars showed that the fibrous structure of GP began to be lost during torrefaction.

### 3.4. Thermal behaviour of chars

#### 3.4.1. Thermal behaviour under inert atmosphere

Thermal degradation behaviour of grape pomace and chars was investigated by thermogravimetry. Fig. 2 shows the TG/DTG profiles of grape pomace and chars. The slight weight loss from the GP that occurred at temperatures below  $128\text{ }^{\circ}\text{C}$  is attributed to evaporation of moisture and volatilization of small organic molecules. Main degradation occurs at temperatures between 200 and  $483\text{ }^{\circ}\text{C}$ . Hemicellulose started to decompose around  $200\text{ }^{\circ}\text{C}$  and reached the maximum weight loss rate at  $273\text{ }^{\circ}\text{C}$ . The hemicellulose peak overlapped with cellulose decomposition and the shoulder around  $323\text{ }^{\circ}\text{C}$  is attributed to the cellulose degradation. The broad peak centered at  $418\text{ }^{\circ}\text{C}$  corresponds to thermal decomposition of lignin. From the curves, it can be seen that the degradation behavior of GP changed significantly after hydrothermal carbonization. For HTC-175-30 and HTC-225-30, degradation occurs over a wider temperature range, with only one main peak being observed. The one wide peak at  $350\text{ }^{\circ}\text{C}$  is indicative that most of the weight loss is related to cellulose and lignin. It is interesting that HTC-275-30 is consistent with the defined two peaks in the temperature range  $152\text{--}517\text{ }^{\circ}\text{C}$ . The second peak (at  $417\text{ }^{\circ}\text{C}$ ) is corresponding to mainly degradation of lignin. The first peak (at  $242\text{ }^{\circ}\text{C}$ ) may be corresponding to degradation of repolymerization products, which formed through hydrothermal degradation at high temperature. These repolymerization products remained in the hydrochar also affected the combustion characteristics of char (this will be discussed in Section 3.4.2). It has to be also noted that the rate of the weight loss of HTC-GP-275-30 was smaller than that of

other chars and raw material. From TG/DTA results, it can be concluded that the hydrothermal treatments at  $175\text{ }^{\circ}\text{C}$  and  $225\text{ }^{\circ}\text{C}$  led to only degradation of hemicellulose, whereas hydrothermal treatment at  $275\text{ }^{\circ}\text{C}$  caused the degradation of cellulose besides hemicellulose. In addition, re-polymerization of primary degradation products took place at this temperature.

#### 3.4.2. Thermal behaviour under air atmosphere

Thermogravimetric analysis under air atmosphere was employed in order to reveal information about the combustion behaviour of chars. As previously shown by other researchers (Ghetti et al., 1996; Miranda et al., 2011), the combustion processes took place in two main stages (the weight loss up to  $150\text{ }^{\circ}\text{C}$  is attributed to the moisture loss) where in the first stage loss of volatile compounds occurred and in the second stage higher molecular weight compounds and char oxidation occurred. It was suggested that the extent of the second combustion step was correlated with lignin content (Ghetti et al., 1996). After second combustion step ( $>543\text{ }^{\circ}\text{C}$ ), decomposition and/or reduction of inorganics took place (Miranda et al., 2011). For hydrochars, first peaks moved towards higher temperature, whereas second peak moved towards lower temperature in comparison to feedstock. It is worthy nothing that only one main DTG peak with a shoulder was observed for H-275-30. This is attributed to low volatile matter and high fixed carbon. For pyrochar T-300-30, the first peak occurred around  $302\text{ }^{\circ}\text{C}$  same as in the feedstock, however the second peak moved towards lower temperature as in hydrochar. For H 250-30, H 275-30 and T-300-30, char combustion rates are higher than that of the volatilization. It is clearly understood that char oxidation took place easily and faster as the fixed carbon and homogeneity increased in fuel.

Table 2 shows the combustion parameters derived from DTG and TGA graphs. The ignition and burnout temperature was determined according to reference (He et al., 2013). The ignition temperature was calculated based on the temperature at which the DTG had its peak value and the corresponding slope to the intersection with respect to the TG profile. Burnout temperature is the temperature at which the rate of weight loss becomes smaller than  $1\text{ wt\%/min}$ .

Because of high volatile matter content, the ignition temperatures of GP are lower than that of chars. As the volatile matters content decreased, the ignition temperature of chars (except H-275-30) increased. Similar observations were made by other researchers for combustion of chars, such as hydrochar from coconut fiber and Eucalyptus leaves (Liu et al., 2012) and palm empty fruit bunches (Parshetti et al., 2013).

The lower ignition temperature of H-275-30 can be explained with the formation of new volatile compounds which remained in the char under hydrothermal carbonization at  $275\text{ }^{\circ}\text{C}$ . For H-250-30 and H-275-30 hydrochars, burnout temperature which gives information about residence time of fuel is smaller than that of GP and other chars. This indicates that the residence time of these chars might be lower than that of the other feedstock in the co-combustion process.

The combustion reactivity of biomass and derived chars is suggested to be directly proportional to the maximum combustion rate and inversely proportional to the corresponding peak temperature (Miranda et al., 2011). Thus;  $\text{Reactivity} = 100 \times \text{maximum combustion rate/peak temperature}$ .  $R_m$  values in the table represent an average reactivity. Among the chars analysed, hydrochars H-175-30, H-200-30 and H-225-30 have higher combustion reactivity in comparison to feedstock (GP). In contrast, the reactivity of hydrochars H-250-30 and H-275-30 was lower than that of other hydrochars and feedstock. This result confirms that the lower lignin content leads to higher reactivity (Ghetti et al., 1996). On the other hand, the chars having lowest reactivity were obtained by torrefaction. The reason might that dry torrefaction produced more

**Table 2**

Combustion parameters of chars.

|          | Peak temperature (°C) | Max. combustion rate (%/min) | Burnout temperature (°C) | $R_m$ (% min <sup>-1</sup> K <sup>-1</sup> ) | Ignition temperature (°C) | Reactivity (% min <sup>-1</sup> K <sup>-1</sup> ) |
|----------|-----------------------|------------------------------|--------------------------|----------------------------------------------|---------------------------|---------------------------------------------------|
| GP       | 97;302;512            | 1.36;9.05;5.81               | 562                      | 5.62                                         | 212                       | 2.99                                              |
| H-175-30 | 72;332;502            | 1.01;9.71;7.55               | 572                      | 5.83                                         | 242                       | 2.92                                              |
| H-200-30 | 80;330;485            | 0.79;10.57;8.35              | 575                      | 5.91                                         | 255                       | 3.20                                              |
| H-225-30 | 73;328;468            | 0.88;9.90;8.42               | 569                      | 6.07                                         | 253                       | 3.01                                              |
| H-250-30 | 71;326;441            | 0.56;7.02;11.56              | 551                      | 5.56                                         | 261                       | 2.62                                              |
| H-275-30 | 68;318;428            | 0.51;5.76;11.19              | 553                      | 5.18                                         | 248                       | 2.61                                              |
| T-250-30 | 91;327;511            | 0.79;7.30;6.75               | 576                      | 4.53                                         | 251                       | 2.23                                              |
| T-300-30 | 87;302;482            | 1.01;3.65;8.28               | 602                      | 4.23                                         | 262                       | 1.72                                              |

**Table 3**

Antioxidant activity of aqueous phases from HTC.

| Aqueous phase sample | Antioxidant activity (ppm GAE) |
|----------------------|--------------------------------|
| H-175-30             | 154                            |
| H-225-30             | 195                            |
| H-275-30             | 157                            |

carbonized char than hydrothermal process or/and high inorganic content in pyrochar.

It might be expected that the inorganic species may have a catalytic effect on the combustion of chars resulting in lower ignition temperature and/or higher reactivity. In contrast to previous studies (Miranda et al., 2011; Haykiri-Acma 2003; Huang et al., 1998), in this study, mineral matter in grape pomace had no considerable effect on lowering the ignition temperature or increase in reactivity.

### 3.5. Antioxidant activity of aqueous phases from hydrothermal carbonization

As known, the waste aqueous phase (WAP) from HTC is one of the main drawbacks of hydrothermal process. In order to overcome this problem, WAP should be treated to reduce the amount of organics before discharge. On the other hand, WAP may contain potentially valuable chemicals. The recovery of these chemicals would improve the economics of the overall process.

The grapes are the major dietary source of polyphenols which have health-promoting effects due to their antioxidant characteristics. Grape pomace (GP) also contains high amount of phenolics due to an incomplete extraction during the winemaking process (Fontana et al., 2013). The solvents such as methanol, ethanol, acetone, water and their mixture have been tested for the extraction of polyphenols from GP. Aliakbarian et al., have used subcritical water for the extraction of polyphenols, flavonoids from grape pomace (Aliakbarian et al., 2012). At the optimum operating condition (140 °C and 11.6 MPa), 31.69 mg GAE/g pomace of total polyphenols was recovered. As based on their study, the antioxidant activity (AA) of aqueous phases obtained from hydrocarbonization was investigated.

As seen from Table 3 increasing extraction temperature from 175 to 250 °C significantly enhanced the AA. This behavior might be due to effect of temperature on the polarity of water (e.g. dielectric constant), because the dielectric constant of water is considerably decreased by increasing the temperature. This result is in agreement with previous studies relating to subcritical water extraction of plants and fruits (Aliakbarian et al., 2012; Singh et al., 2011). The decrease in AA above 250 °C might be due to the degradation of flavonoids and anthocyanins at high temperatures. As conclusion, one can conclude that grape pomace can be converted to not only solid fuel but also chemicals through hydrothermal carbonization.

## 4. Conclusion

HTC yielded a higher energy densification and higher energy yield than torrefaction. IR spectra of hydrochars demonstrated that decomposition of hemicelluloses occurred at lower temperatures (175 °C) whereas cellulose started to decompose at temperatures higher than 250 °C. Torrefaction produced pyrolytic chars having more aromatic nature than hydrochars. Due to the dissolution of inorganics under the hydrothermal conditions, a significant decrease in ash content of chars was obtained. HTC produced the char having higher combustion reactivity compared to torrefaction. Another advantage of HTC is the fact that aqueous phase (a waste from hydrothermal process) showed antioxidant activity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2014.03.052>.

## References

- Aliakbarian, B., Fathi, A., Perego, P., Dehghani, F., 2012. The journal of supercritical fluids extraction of antioxidants from winery wastes using subcritical water. *J. Supercrit. Fluids* 65, 18–24.
- Almeida, G., Brito, J.O., Perre, P., 2010. Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: the potential of mass loss as a synthetic indicator. *Bioresour. Technol.* 101, 9778–9784.
- Arias, B., Pevida, C., Fermo, J., Plaza, M.G., Rubiera, F., Pis, J.J., 2008. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Process. Technol.* 89, 169–175.
- Bates, R.B., Ghoniem, A.F., 2012. Biomass torrefaction: modeling of volatile and solid product evolution kinetics. *Bioresour. Technol.* 124, 460–469.
- Brand-Williams, Cuvelier, W., Berset, M.E.C., 1995. Use of a free radical method to evaluate antioxidant activity. *LWT—Food Sci. Technol.* 28 (1), 25–30.
- Bridgeman, T.G., Jones, J.M., Shield, I., Williams, P.T., 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* 87, 844–856.
- Cao, X., Ro, K.S., Chappell, M., Li, Y., Mao, J., 2011. Chemical structures of swine-manure chars produced under different carbonization conditions investigated by advanced solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy. *Energy Fuels* 25, 388–397.
- Channiwala, S.A., Parikh, P.P., 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81 (8), 1051–1063.
- Ciolkosz, D., Pennsylvania, T., Wallace, R., Hamilton, B.A., 2011. A review of torrefaction for bioenergy feedstock. *Biofuels Bioprod. Biorefin.* 3, 317–329.
- Dai, J., Sokhansanj, S., Grace, J.R., Bi, X., Lim, C.J., Melin, S., 2008. Overview and some issues related to co-firing biomass and coal. *Can. J. Chem. Eng.* 86, 367–386.
- Fontana, A.R., Antoniolli, A., 2013. Grape pomace as a sustainable source of bioactive compounds: extraction, characterization, and biotechnological applications of phenolics. *J. Agric. Food Chem.* 61, 8987–9003.
- Funke, A., Ziegler, F., Berlin, T.U., 2010. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod. Biorefin.* 4, 160–177.
- Ghani, W.A.W.A.K., Mohd, A., da Silva, G., Bachmann, R.T., Taufiq-Yap, Y.H., Rashid, U., Al-Muhtaseb, A.H., 2013. Biochar production from waste rubber-wood-

- sawdust and its potential use in C sequestration: chemical and physical characterization. *Ind. Crops Prod.* 44, 18–24.
- Ghetti, P., Ricca, L., Angelini, L., 1996. Thermal analysis of biomass and corresponding pyrolysis products. *Fuel* 75, 565–573.
- Haykiri-Açma, H., 2003. Combustion characteristics of different biomass materials. *Energy Convers. Manag.* 44, 155–162.
- He, C., Giannis, A., Wang, J.-Y., 2013. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior. *Appl. Energy* 111, 257–266.
- Hoekman, S., Broch, A., Robbins, C., 2011. Hydrothermal carbonization (HTC) of lignocellulosic biomass. *Energy & Fuels* 25, 1802–1810.
- Huang, M., Li, X., 1998. Thermal degradation of cellulose and cellulose esters. *J. Polym. Sci.* 68, 293–304.
- Kang, S., Li, X., Fan, J., Chang, J., 2012. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, D-xylose, and wood meal. *Ind. Eng. Chem. Res.* 51, 9023–9031.
- Lee, J.-W., Kim, Y.-H., Lee, S.-M., Lee, H.-W., 2012. Optimizing the torrefaction of mixed softwood by response surface methodology for biomass upgrading to high energy density. *Bioresour. Technol.* 116, 471–476.
- Libra, J.A., Ro, K.S., Kamman, C., Funke, A., Berge, N.D., York Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., Kern, J., Emmerich, K.-H., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* 2 (1), 89–124.
- Liu, Z., Quek, A., Hoekman, S.K., Srinivasan, M.P., Balasubramanian, R., 2012. Bioresource technology thermogravimetric investigation of hydrochar-lignite co-combustion. *Bioresour. Technol.* 123, 646–652.
- Liu, Z., Quek, A., Kent Hoekman, S., Balasubramanian, R., 2013. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *Fuel* 103, 943–949.
- Lu, X., Jordan, B., Berge, N.D., 2012. Thermal conversion of municipal solid waste via hydrothermal carbonization: comparison of carbonization products to products from current waste management techniques. *Waste Manag.* 32, 1353–1365.
- Medic, D., Darr, M., Shah, A., Potter, B., Zimmerman, J., 2012. Effects of torrefaction process parameters on biomass feedstock upgrading. *Fuel* 91, 147–154.
- Miranda, M.T., Arranz, J.I., Román, S., Rojas, S., Montero, I., López, M., Cruz, J.A., 2011. Characterization of grape pomace and pyrenean oak pellets. *Fuel Process. Technol.* 92, 278–283.
- Mumme, J., Eckervogt, L., Pielert, J., Diakité, M., Rupp, F., Kern, J., 2011. Hydrothermal carbonization of anaerobically digested maize silage. *Bioresour. Technol.* 102, 9255–9260.
- Parshetti, G.K., Kent Hoekman, S., Balasubramanian, R., 2013. Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. *Bioresour. Technol.* 135, 683–689.
- Prins, M.J., Ptasiński, K.J., Janssen, F.J.J.G., 2006. Torrefaction of wood Part 1. Weight loss kinetics. *J. Anal. Appl. Pyrolysis* 77, 28–34.
- Román, S., Nabais, J.M.V., Laginhas, C., Ledesma, B., González, J.F., 2012. Hydrothermal carbonization as an effective way of densifying the energy content of biomass. *Fuel Process. Technol.* 103, 78–83.
- Sevilla, M., Maciá-Agulló, J.A., Fuertes, A.B., 2011. Hydrothermal carbonization of biomass as a route for the sequestration of CO<sub>2</sub>: chemical and structural properties of the carbonized products. *Biomass Bioenergy* 35, 3152–3159.
- Singh, P.P., Saldana, M.D.A., 2011. Subcritical water extraction of phenolic compounds from potato peel. *Food Res. Int.* 44, 2452–2458.
- Titirici, M.-M., Thomas, A., Antonietti, M., 2007. Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO<sub>2</sub> problem? *New J. Chem.* 31, 787–789.
- Yan, W., Acharjee, T.C., Coronella, C.J., Va, V.R., 2009. Thermal pretreatment of lignocellulosic biomass. *Environ. Prog. Sustainable Energy* 28 (3), 435–440.
- Yu, J., Ahmedna, M., 2013. Functional components of grape pomace: their composition, biological properties and potential applications. *Int. J. Food Sci. Technol.* 48, 221–237.